

Time Dependent Density Functional Theory Calculations of Large Compact PAH Cations: Implications for the Diffuse Interstellar Bands

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ABSTRACT

We investigate the electronic absorption spectra of several maximally peri-condensed polycyclic aromatic hydrocarbon radical cations with time dependent density functional theory calculations. We find interesting trends in the vertical excitation energies and oscillator strengths for this series containing pyrene through circumcoronene, the largest species containing more than 50 carbon atoms. We discuss the implications of these new results for the size and structure distribution of the diffuse interstellar band carriers.

Subject headings: astrochemistry — ISM: molecules — methods: analytical

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are commonly accepted as being ubiquitous in the interstellar medium (ISM). They have received considerable attention in recent years as possible carriers of the diffuse interstellar bands (DIBs), after the presentation of the PAH hypothesis (Crawford et al. 1985; van der Zwet and Allamandola 1985; Leger and d'Hendecourt 1985; Salama et al. 1996, 1999). There have been many studies both experimental and theoretical, on various types of PAHs that may be DIB carriers, and that may be most likely to exist in the ISM (for some example references, see Salama et al. (1994, 1995); Joblin et al. (1999); Romanini et al. (1999); Brechignac and Pino (1999); Weisman et al.

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(2001)). PAH cations, both radical and closed-shell, are good candidates for DIB carriers. Not only do they have electronic absorptions in the spectral region of interest, but they additionally have high ionization energies, a requirement to survive in the ISM (Sonnentrucker et al. 1997).

Theoretical predictions of PAH absorption spectra are a useful tool in the search for DIB carriers. Ideally, gas-phase spectroscopy in the laboratory is necessary to be able to match accurately a potential DIB carrier to astrophysical data. However, current experimental difficulties in sample preparation have inhibited direct gas phase spectroscopy of larger PAHs, and most studies have been performed in rare gas matrices. Although recent studies (Romanini et al. 1999; Brechignac and Pino 1999; Biennier et al. submitted 2002) have provided the first electronic spectra of PAH ions in the gas phase, to our knowledge, absorption results have not yet been published for medium to large sized PAHs in the gas-phase (i.e. PAHs containing more than 20 carbon atoms). In this regard, calculated spectra are potentially useful in guiding future experimental work. Calculated spectra are also valuable in terms of gaining a better understanding of the nature of the transitions (Gutman and Cyvin 1989).

Time dependent density functional theory (Runge and Gross 1984; Petersilka et al. 1996) methods are capable of predicting vertical excitation energies and oscillator strengths for relatively large molecules (for example, see Weisman et al. (2001)). Excitation energy accuracy is possible with conventional exchange-correlation functionals to within less than a third of an electron volt (eV) for radical cations such as pyrene (Hirata et al. 1999). The ability to predict oscillator strengths is also quite useful. Our experience is that oscillator strength predictions are in qualitative accord with experimental observation (Hirata et al. 1999).

In a recent study, we have found an interesting trend in oscillator strengths within the perylene, terrylene, quaterrylene series (Halasinski et al. submitted 2002). The bright state for each of these molecules is a transition of dipole symmetry along the long axis of the molecule. Since the dipole forms along the long axis, the oscillator strength of the bright state increases as the molecular backbone grows in length from perylene to terrylene to quaterrylene. This results in a net increase in oscillator strength per unit mass of carbon along this series. Such a conclusion could not be easily made without TDDFT calculations, since an oscillator strength is very difficult to quantify in the only experimental techniques that have so far been used to study these species, namely matrix-isolation spectroscopy.

This information has potentially significant astrophysical implications. A larger oscillator strength per unit mass of carbon for larger molecules could certainly shift the search for DIB carriers towards larger species if this trend holds for PAHs other than just this one oligorylene series. This is what we aim to find out by studying the oscillator strength

trends in more PAH series. In this letter, we have chosen to investigate a series of maximally pericondensed PAH radical cations. Maximally pericondensed PAHs are those PAHs that have the largest number of carbon atoms for a given number of hydrogen atoms. These PAHs have received much attention since they are expected to be especially stable structures (Stein 1978) and the likely precursors to soot formation in hydrocarbon flames (Frenklach and Feigelson 1989; Cherchneff and Barker 1992).

2. ELECTRONIC STRUCTURE METHODS

All calculations were performed with the Q-Chem quantum chemistry program package (Kong et al. 2000) on IBM RS/6000 workstations. The following PAH radical cations were investigated: pyrene ($C_{16}H_{10}$), coronene ($C_{24}H_{12}$), ovalene ($C_{32}H_{14}$), circumpyrene ($C_{42}H_{16}$), and circumcoronene ($C_{54}H_{18}$). See Figure 1 for oriented structures. All ground state geometries were optimized using density functional theory with Becke exchange (Becke 1988) and LYP correlation (Lee et al. 1988), and the 6-31G* basis set. The geometries were confirmed to be minima by calculation of the Hessian matrix.

The vertical excitation energies and oscillator strengths were determined using time dependent density functional theory (TDDFT) at the BLYP/6-31G* level. Radical cation excitation energies are generally insensitive to basis set size for TDDFT calculations (for example, see Halasinski et al. (submitted 2002)), so we believe the 6-31G* basis is sufficient. Commonly used LDA and GGA functionals perform well for predicting the energies of valence states, but perform quite poorly for Rydberg states (Casida et al. 1998; Tozer and Handy 1998; Hirata and Head-Gordon 1999). However, we roughly estimate the onset of the Rydberg level as the negative of the highest occupied Kohn-Sham orbital (Casida et al. 1998), which falls in the range of 7-9 eV for the PAH radical cations in this study. Our reported excitation energies remain well below this level.

3. RESULTS AND DISCUSSION

The PAH radical cation calculations in this investigation have all been run with D_{2h} molecular symmetry. Neutral coronene and circumcoronene have D_{6h} molecular symmetry, however the radical cation derivatives are expected to experience Jahn-Teller effects and distort to D_{2h} symmetry (Kato et al. 1999). We orient the pyrene radical cation in the xy plane with the long axis along the x axis. All other molecules contain a central 'pyrene-like' unit with the same orientation, so that for larger molecules like ovalene, the long axis

is actually in the y direction. The coronene and circumcoronene D_{2h} structures are very slightly elongated in the y direction.

We focus on the brightest transitions of the series, that is, the electronic excitations with the largest oscillator strengths. These are the transitions with most promise for correlation with the DIBs (Salama et al. 1996, 1999). We present the strongest excitation of B_{2u} and B_{3u} transition symmetry. The transition symmetry is the product of the ground state and excited state symmetries, and is a simpler way to characterize the transitions in these molecules, since the ground state symmetries are different. In the xy plane orientation described earlier, the B_{2u} and B_{3u} transitions are oriented along the y and x axes, respectively.

Table 1 shows the bright transitions for the pyrene, coronene, ovalene, circumpyrene and circumcoronene radical cations. It is interesting to note that coronene and circumcoronene do not seem to fit into a trend with the other radical cations. The B_{2u} excitation is lower in energy than the B_{3u} excitation for all of the molecules. However, the transition with the larger oscillator strength is not the same for all five species. B_{3u} is the stronger absorption for pyrene, ovalene and circumpyrene, while B_{2u} is the stronger absorption for coronene and circumcoronene.

These new theoretical results confirm the previous findings regarding the general spectral characteristics of PAH ions (Salama et al. (1996), and references therein). They show that the visible absorption spectra of pericondensed PAH ions are indeed dominated by one transition although the relative intensities can differ among different subfamilies. They also provide, for the first time, precise information about the nature of the molecular transitions as well as important input into the quantitative variation of the oscillator strengths with the molecular structure of the PAH ions. Oscillator strengths are key parameters for astrophysical models because they dictate the abundance of cosmic carbon that needs to be locked-up in any specific molecular carrier, and, hence, its plausibility as an interstellar band carrier. Armed with these new results, one can now fine-tune the theoretical predictions that were made in previous astrophysical models (Salama et al. 1996).

It is clear that circumpyrene behaves similarly to pyrene, and likewise circumcoronene mirrors coronene. Let us refer to the pyrene-circumpyrene pair as the pyrene series, and the coronene-circumcoronene pair as the coronene series. The next larger member of these homologous series is then defined by adding benzene rings to completely enclose circumpyrene and circumcoronene, analogous to the way that circumpyrene and circumcoronene were formed from pyrene and coronene, respectively.

In both the pyrene and coronene series, the larger species has an excitation energy roughly 0.6 eV lower than the smaller species for the B_{2u} transition, and 1 eV lower for the

B_{3u} transition. Additionally, the oscillator strength of the larger species in relation to the smaller species increases for the B_{2u} transition and decreases for the B_{3u} transition. The pyrene series strong absorption (B_{3u}) becomes weaker for larger members, so the oscillator strength per unit mass of carbon quickly decreases. The B_{2u} absorption does grow stronger for larger members, however it is fairly weak to begin with and the excitation energy itself decreases rapidly out of the range of the known DIBs. The situation is similar for the coronene homologous series, except that the B_{3u} absorption is not strong. We will discuss these trends further later.

Ovalene behaves similarly to pyrene and circumpyrene. In comparison to circumpyrene, ovalene's oscillator strength increases more relative to pyrene for the B_{2u} transition and decreases more from pyrene for the B_{3u} transition. This is most likely due to the fact that the long axes for ovalene and circumpyrene are switched, that is ovalene's long axis is the y axis, and so the B_{2u} transition is stronger than circumpyrene's, and visa versa for the B_{3u} transition. Overall, ovalene seems closer to the pyrene series than the coronene series, however it is not part of a homologous series in either case so we will not pursue it further in this discussion except to emphasize that all compact PAHs may not be grouped together for purposes of predicting oscillator strength trends.

Let us consider the pyrene series and coronene series further now. We have already seen that the oscillator strength of the B_{2u} transition decreases along both homologous series and the strength of the B_{3u} absorption increases. What is even more important to consider in the context of the interstellar carbon budget, is the oscillator strength per unit mass of carbon. Table 2 shows the oscillator strength and oscillator strength per unit mass of carbon for both transitions. We can now see that while the oscillator strength itself increases for the B_{3u} transition, the oscillator strength per unit mass of carbon does not. In other words, the species in these series grow in size faster than the strength of their absorptions. Thus the oscillator strength per unit mass of carbon decreases for both of the strongest absorptions in the pyrene series and the coronene series.

The results for these two series of PAH radical cations show trends that would seem to argue against larger molecules of these series as promising candidates for DIB carriers, despite their stable structures. With the exceptions of coronene and circumcoronene, these PAH radical cations do exhibit transitions of strong oscillator strength. However, these strong transitions decrease per unit mass of carbon along the series and except for pyrene, are not comparable to the perylene series. For example, the oscillator strength per unit mass of carbon for quaterylene's strongest absorption is approximately eight times larger than circumcoronene's strongest absorption. This would require almost 10 times more circumcoronene in the interstellar medium than quaterylene to yield a signal of the same

magnitude. Additionally, the excitation energies of the pyrene and coronene series B_{2u} transitions decrease rapidly out of the range of the known DIB region (roughly 1.0 - 3.1 eV).

4. CONCLUSIONS

We have presented calculated absorption spectra of several pericondensed PAH radical cations in this letter. Time dependent density functional theory methods allow for the investigation of larger molecules than are readily feasible with other ab initio electronic structure methods. We have studied the first five maximally pericondensed PAH radical cations: pyrene, coronene, ovalene, circumpyrene, and circumcoronene.

We have found interesting and insightful trends in the oscillator strength per unit mass of carbon for two series of pericondensed PAH radical cations. First, we have identified the fact that oscillator strength trends must be addressed in specific homologous series only. It is not appropriate to generalize trends for all compact or non-compact PAHs together because they may behave very differently. We have identified two homologous series within the maximally pericondensed PAHs family, namely the pyrene series and coronene series, which are grouped with their circum- counterparts. These two series differ in that the strongest absorption is along the x axis for pyrene (B_{3u}) and along the y axis for coronene (B_{2u}). However, both series exhibit the behavior that the two strongest absorptions in the DIBs spectral region decrease in oscillator strength per unit mass of carbon along the series.

We therefore find the pyrene and coronene radical cation series to be poor candidates for carriers of the diffuse interstellar bands in comparison to strong absorbers like the oligorylene series, although pyrene itself is still a possible candidate. The decreasing oscillator strength per unit mass of carbon and rapidly decreasing excitation energy both contribute unfavorably to the possibility of these compact PAHs being DIBs carriers. We should note that we have confined our study to the brightest states of roughly the visible region of the spectrum, which is the spectral region of interest for the known DIBs. There certainly exist higher lying excited states for these PAHs that absorb in the UV and are simply out of the energetic range of the known DIBs.

Our results have specific implications for future work. We have identified that different series of compact PAHs behave differently from each other. It seems appropriate that future effort should be directed to study the oscillator strengths of a variety of PAH homologous series in the hope of identifying both good and bad candidates for the DIBs carriers to aid in the direction of future laboratory investigations. We aim to do this in follow up papers.

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy, under Contract No. DE-AC03-76SF00098 and a grant from the Petroleum Research Fund. We additionally acknowledge grants of supercomputer time from NERSC, and a SUR grant from IBM for computing equipment. MHG is on appointment as a Miller Research Professor in the Miller Institute for Basic Research in Science.

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Table 1: Pericondensed Series Brightest Electronic Transitions of B_{2u} and B_{3u} Symmetry^a

Radical Cation	B_{2u} Transition			B_{3u} Transition		
		Energy	OS		Energy	OS
Pyrene	${}^2B_{3g} \rightarrow {}^2B_{1u}$	1.5923	(0.0156)	${}^2B_{3g} \rightarrow {}^2A_u$	2.9223	(0.2019)
Coronene	${}^2B_{1u} \rightarrow {}^2B_{3g}$	1.6481	(0.0473)	${}^2B_{1u} \rightarrow {}^2B_{2g}$	2.8391	(0.0267)
Ovalene	${}^2B_{2g} \rightarrow {}^2A_u$	1.1801	(0.0293)	${}^2B_{2g} \rightarrow {}^2B_{1u}$	2.1110	(0.1319)
Circumpyrene	${}^2B_{1u} \rightarrow {}^2B_{3g}$	0.9898	(0.0263)	${}^2B_{1u} \rightarrow {}^2B_{2g}$	1.9779	(0.1466)
Circumcoronene	${}^2B_{3g} \rightarrow {}^2B_{1u}$	1.0108	(0.0660)	${}^2B_{3g} \rightarrow {}^2A_u$	1.8925	(0.0262)

^aBLYP/6-31G**//BLYP/6-31G* excitation energies in eV, oscillator strengths (OS) given in parentheses.

Table 2: Oscillator Strength (OS) Trends of Pericondensed Transitions of B_{2u} and B_{3u} Symmetry

Radical Cation	No. of Carbon Atoms	B_{2u} Transition		B_{3u} Transition	
		OS	OS/Carbon*1000	OS	OS/Carbon*1000
Pyrene	16	0.0156	0.98	0.2019	12.6
Circumpyrene	42	0.0263	0.63	0.1466	3.49
Coronene	24	0.0473	1.97	0.0267	1.11
Circumcoronene	54	0.0660	1.22	0.0262	0.49

Fig. 1.— Oriented Structures of the Pericondensed PAH Radical Cations: ^{a)}Pyrene, ^{b)}Coronene, ^{c)}Ovalene, ^{d)}Circumpyrene, and ^{e)}Circumcoronene.

